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13. ABSTRACT *(Maximum 200 Words)*

This report summarizes the research work done during the period covered by the AFOSR grant. The PI investigated the flow-orientation coupling and pattern formation in flows of liquid crystalline polymers. Both short and long range elasticity due to the microstructure formation in the macromolecular material can impact on the flow stability. Various experimental phenomena have been modeled by the hydrodynamic theory developed in the project. Several new theories for polymer-liquid crystal polymer mixtures and polymer-clay nanocomposites have been developed providing a solid foundation for the next phase of study on the macromolecular fluids.

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This report summarizes the research activities, partially supported by AFOSR, conducted during the period of Oct. 15, 1998–Oct. 14, 2001. A list of articles published and accepted for publication in the supported period is supplied at the end of the report.

During this period, my research activities have been centered around modeling and computation of flows of liquid crystal polymers as well as their potential applications in military use. The scientific issues we have been pursuing are more or less related to understanding of the flow orientation coupling in the macromolecular fluids in various flow fields. Specifically, we studied how microstructure affects the transient flow stability in free surface filament flows, how flow orientation coupling creates signatures in defect formation and how spatial structure separation in equilibrium order parameters and directors creates multidimensional, spatially nonhomogeneous patterns and their coupling under the influence of nontrivial flow fields. In addition, I have also been involved in the development of hydrodynamic theories for flows of nanocomposites including mixtures of polymers and liquid crystalline polymers lately. These new nanocomposites are very promising materials. Their physical properties and dynamical behavior need to be understood theoretically. The new hydrodynamic theories that I have developed provide the much needed theoretical framework to attain the theoretical understanding of the complex fluids. The detailed analysis of the theories and experimental validation will be the focus of the next phase of research.

1. Special liquid filament flows of LCPs and their stability

Traditionally, the capillary instability of an equilibrium cylindrical filament of a fluid with constant radius is used to predict the onset of the filament breakup and selection of droplet sizes. Lately, new contracting/expanding filament solutions are found for falling liquid filaments in a variety of free surface liquid filament models. Consequently, one's understanding of liquid filament motion in transient is augmented significantly by analyzing the transient special liquid filaments. These special liquid filaments are of particular importance to polymeric liquid materials since experiments show the polymeric liquid filament often experiences a significant thinning process before it breaks.

Using an ad hoc low dimensional model, we studied the prolonged thinning phenomenon for filaments of liquid crystal polymers by focusing on exact, special filament solutions of the governing equation system for liquid crystal polymers. Our analysis reveals that the prolonged or sustained thinning is related to the internal molecular orientation during the transient process. So long as a sizable amount of the negative first normal stress difference is sustained by the internal molecular orientation, the thinning process will persist without being disrupted by instabilities. This finding suggests that the liquid crystal polymer material to be processed can be pre-processed to attain certain orientational order before it is processed in an elongational device. This conclusion is also consistent with our studies of fiber spinning processes, where high throughput was observed in liquid crystal liquids with relatively low degree of orientation upstream.

For sufficiently thin filaments, our study still predicts instability in the range of both long and short waves, indicating the ultimate catastrophic fate of a falling liquid filament regardless its material properties. This work is published in J. of Non-Newtonian Fluid Mechanics.

2. Spatially nonhomogeneous patterns

Liquid crystal polymers are capable of forming a large number of orientation patterns. Previous theoretical studies have been limited on the homogeneous patterns and transient patterns related to the spinodal decomposition. With an extended Doi type theory, we are able to find several families of periodic patterns that vary spatially in 1 to 3 dimensional space analytically. These orientation patterns reveal a great deal more about the capacity of the Doi theory and the interaction between the flow field and the orientation. Currently, we are looking into the variation of the spatial orientational structure under the perturbation

of flow fields, in particular, shear flows. We hope this study will elevate our understanding on complex dynamics observed in nontrivial flows of LCPs and lead to improvement in our future modeling endeavor of the microstructural material.

With the coupling of the flow and orientation in the Doi model, we also analyzed the defect structure in biaxially stretching elongational flows and found a correlation between the hydrodynamics pressure and the orientational defects in the material. These theoretical studies provide invaluable insight into the flow-orientation coupling in the dynamics modeled by the extended Doi type theory. The works are performed jointly with M. G. Forest of UNC and Dr. Hong Zhou of UC Santa Cruz. A few papers published are related to these studies.

3. Constrained nonisothermal theories for viscous fluids and their linear stability

The PI analyzed the illposedness due to Hadamard instability at any rest state in the non-isothermal constrained theory for viscous fluids developed by Cao et. al. In collaboration with F. Rooney (UC, Berkeley), Steve Bechtel (OSU) and M. G. Forest (UNC), we proposed various regularization mechanisms to regularize the illposed theory. For example, we found the constrained theory with prescribed density-entropy dependence is well-posed while the one with prescribed density-temperature dependence is illposed. This thereby established the frame work for selecting appropriate continuum models for modeling nonisothermal phenomena of viscous liquids. This work will also impact significantly on our studies of weakly compressible materials as most of polymeric materials are.

4. A new hydrodynamic theory for nonhomogeneous liquid crystal polymers

Motivated by the need to study flows of discotic LCPs, the PI developed a hydrodynamic theory for flows of LCPs of spheroidal shapes, in which the shape of the molecule is modeled by a scalar shape parameter related to the aspect ratio of the spheroid. This new theory incorporates the geometric effect of the molecular shape into the stress expression and the intermolecular potential so that it can be applied to both rodlike LCPs and discotic LCPs at the two extremes of aspect ratios. This theory reduces to the Leslie-Ericksen theory in the torque balance equation with three distinct elastic moduli and extends the LE stress tensor to higher orders in weak flow limit. The enhanced polymer viscosity in the discotic LCP is effectively accounted for. It also captures the ordering change in the elastic moduli in different regimes of aspect ratios and concentration. This theory has been used in study

of flow behavior for discotic liquid crystal polymers and extended to nanostructured flowing materials with clay particles of spheroidal shapes. The work has been submitted to Journal of Chemical Physics for publication.

5. Study of flow-orientation interaction in shearing flows of rodlike liquid crystal polymers

In flows of LCPs, due to the development of inhomogeneities in the microstructure, it may induce secondary flows to affect the overall flow behavior significantly. In this project, we study the flow orientation coupling in a shear flow geometry. First, we investigate the coupling in one spatial dimension across the shearing plates. Our findings are quite dramatic. Due to the strong dependence of the stress tensor on the average molecular orientation, the velocity field is drastically altered in the flow field between the shearing plates. The distorted velocity field in the shear flow depends on the magnitude of the distortional elastic energy of the material. When the distortional elastic energy is small, tumbling/wagging behavior prevails; otherwise, the tumbling/wagging may eventually be halted leading to layers of orientation patterns parallel to the flow direction. At sufficiently high "shear rate", the internal orientation prefers the out-of-plane orientation where the major axis of the orientation tensor tends to orient out of the shearing plane. When the orientation prefers out-of-plane, both steady states and transient patterns may form yielding very rich dynamics in the governing equation system. This work is summarized in a paper to be submitted soon.

6. Exact patterns predicted by the Doi-Marrucci-Greco model

Doi-Marrucci-Greco model is a kinetic theory that models both the long and short range elasticity in the nonhomogeneous LCP. The approximate Doi-Marrucci-Greco model resulted from a closure approximation provides the simplest tensor based model for flows of nematic liquid crystal polymers while retaining all the essential ingredients of a more general theory. A detailed analysis on the structure and solution of the model would help us to understand how the various patterns are formed or selected in flowing LCPs. Through a variety of ansatz based on different tricks of separation of variables, we are able to find several families of exact solutions of the governing partial differential equation system. These families of solutions are responsible for the orientation patterns ranging from spatial patterns formed by order parameter variations, director rotation and their combination to cholesteric patterns. The model itself imposes, implicitly, a selection criterion that certain spatial patterns due to the director rotation are not sustainable when the length scale associated to the elastic moduli is

smaller than a threshold number. This inter-relationship between the elastic moduli and the length scale formed in the spatial periodic pattern sheds new light on how textures in LCP materials may be formed in the equilibrium and how the texture scale relates to the material property. This exact patterns may play an important role in our fundamental understanding of the models for LCPs and texture dynamics. The results are reported in a paper appeared in Physica D, which is coauthored with Prof. Forest and Zhou.

7. Hydrodynamic theories for polymer-LCP mixtures

I have developed a hydrodynamic theory for mixtures of polymers and liquid crystalline polymers. This is a kinetic theory can be approximated using closure approximation or GENERIC formalism to obtain tensor based approximate models. In this theory, Brownian motion, excluded volume, long-range molecular interaction, density variation, polymer-LCP interaction are all incorporated. Preliminary studies have shown promising agreement with the experimental findings. Detailed analysis of the theory and its approximations will be my focus in the next phase of research.

8. Hydrodynamic theories for polymer-clay nanocomposites

I extended my work on kinetic theories for LCPs and polymer-LCP mixtures to model polymer-clay nanocomposites. In addition to the important physical effect alluded to above the polymer-LCP mixtures, we also included the clay-clay interaction mediated by the flexible potential which is the intriguing effect for the nanocomposites. A self-consistent mean field method is used to calculate the interaction potential based on the very latest work of Balasz's group at University of Pitts. Further investigate of the theory in shear flows is underway in collaboration with Dr. Richard Vaia's group at WPAFB.

9. Unified hydrodynamic theories for nematic, cholesteric, smectic A and smectic C liquid crystals

This project involves in an ongoing collaboration with Prof. Calderer (University of Minnesota) and Liu (Penn State U.). We are developing a general frame work for flows of liquid crystal polymers that may form a variety of spatial patterns at different temperature, ranging from isotropic phase to smectic phases, including chiral structures using an orientation tensor based formulation. Previous theories focused on the physics of the static phases and are mostly director based that are invalid in the neighborhood of singularities (defects).

Thus, their use in study rheology of LCP flows are quite limited and difficult. This prompted us to seek tensor based theories that can model defects at ease.

We have obtained a unified theory for flows of LCPs capable of handling isotropic, nematic, cholesteric and smectic A phase, including all the phase transitions involved, and modeling the long and short range elasticity of the polymers. Currently, we are analyzing the theory in static and plane shear flows to evaluate its capacity. The success of the theory will provide a solid modeling tool for flows of LCPs exhibiting possibly smectic A phases under certain conditions. The advantage of our theory lies in its easy handling of defects in LCP dynamics.

Independently, the PI has extended the theory to model flows of LCPs forming the smectic C phase and its chiral counterpart smectic C^*. However, lack of manpower in our research team is becoming an acute issue to move the projects forward in a timely fashion.

10. Interaction with WPAFB

During the funded period, I and my collaborator Prof. M. Greg Forest have visited WPAFB several times. We have had discussion sessions with Dr. Richard Vaia and Dr. Benji Maruyama's group on different topics.

We discussed our modeling capacity with discotic LCPs with Dr. Maruyama's group. They are interested in the carbon-fiber in various flow fields, in particular fiber spinning flows. We are pursuing a multi-dimensional simulation of the fiber spinning flow using our hydrodynamic model for discotic lcps. Further contact and exchange information in this project is planned in the future.

Our discussion and the follow-up interactions with Dr. Richard Vaia are centered around polymer-clay nanocomposites. The latest theory development and subsequent studies are more or less motivated by the first meeting with Dr. Vaia and the experimental capacity he demonstrated during our visits. Our collaboration is moving into a substantial stage lately. We are pursuing model studies of shear and slit flows of the nanocomposites and planning comparison and parameter calibration using Vaia's slit flow experiments.

We understand that this is a potentially very important project both academically and technologically. In addition, it would have great potential to put our research results in direct military applications. Therefore, we are very serious about the project and hope to bring it to a level where full-fledged scientific collaboration between the Air force lab and our team can be carried out in a relatively short time scale.

11. List of publications during the period

- 1. S. E. Bechtel, M. G. Forest, Q. Wang and Hong Zhou, "Free Surface Viscoelastic Fibers and Jets", *Advances in the Flow and Rheology of Non-Newtonian Fluids Parts A and B*, Elsevier Science, 1999, pp. 1069–1116.

- 2. Q. Wang and M. G. Forest, "Near-equilibrium dynamics of Doi models for liquid crystal polymer flows: catastrophic and regularized behavior", *Journal of Non-Newtonian Fluid Mechanics* 83 (1999), pp. 131–150.

- 3. M. G. Forest, H. Zhou and Q. Wang, " A model study of the spinning of thermotropic liquid crystalline polymers: fiber performance predictions and bounds on throughput", *Advances in Polymer Technology* 18 (4) (1999), pp. 314–335.

- 4. M. G. Forest, Q. Wang. and H. Zhou, "Nonhomogeneous patterns and core defects in elongational flows of liquid crystalline polymers", *Journal of Rheology* 43 (6) (1999), pp. 1573-1583.

- 5. M. G. Forest, Q. Wang and H. Zhou, "Homogeneous pattern selection and director instabilities of nematic liquid crystal polymers induced by elongational flows", *Physics of Fluids*, 12 (3) (2000), pp. 1-9.

- 6. Q. Wang, "Special cylindrical free surface jets of liquid crystalline polymers and their stability", *Journal of Non-Newtonian Fluid Mechanics*, 90 (2000), pp. 25-45.

- 7. M. G. Forest, H. Zhou and Q. Wang, "Thermotropic liquid crystalline polymer fibers", *Siam Journal on Applied Math*, 60(4) (2000), pp. 1177-1204.

- 8. Q. Wang, "Illposedness in thermomechanically consistent constrained theory for materials with prescribed temperature-dependent density" *Journal of Applied Mechanics*, 67 (2000), pp. 29-32.

- 9. M. G. Forest, Q. Wang and H. Zhou, "Exact banded patterns from a Doi-Marrucci-Greco model of nematic liquid crystal polymers", *Physical Review E*, 61 (6) (2000), pp. 61-69.

- 10. M. G. Forest, Q. Wang. and H. Zhou, "Exact solutions of the extended Doi model and their applications in flows of LCPs", *Physica D* 152-152 (2001), pp. 288-309.

- 11. M. G. Forest, Q. Wang. and H. Zhou, "On the phase diagram for discotic liquid crystals in simple elongational flows", *Liquid Crystals* 28(5) (2001)., pp. 717-720.

- 12. Q. Wang, "The role of Surface Elasticity in Capillary Instability of Cylindrical Jets of Liquid Crystalline Polymers", to appear *Journal of Non-Newtonian Fluid Mechanics*, 2001

12. List of papers accepted or submitted during the period

- 1. F. J. Rooney, S. E. Bechtel, Q. Wang and M. G. Forest, "On the stability of the rest state of Thermomechanically constrained Newtonian Fluids", submitted to *Proc. Roy. Soc. London Ser. A*, 2001.
- 2. Q. Wang, "A hydrodynamic theory of nematic liquid crystalline polymers of different configurations", submitted to *Journal of Chemical Physics*, 2000
- 3. M. G. Forest and Q. Wang, " Monodomain response of finite-aspect-ratio macromolecules in shear and related linear flows", submitted to *Rheological Acta*, 2001
- 4. Qi Wang, "Hydrodynamic theories for mixtures of polymers and rodlike liquid crystalline polymers", submitted to *Physical Review E*, 2001.
- 5. Q. Wang, "A kinetic theory for flows of polymer-clay nanocomposites", submitted to *Macromolecules*, 2001
- 6. Qi Wang, Weinan E, Chun Liu, and Pingwen Zhang, " Kinetic theories for flows of nonhomogeneous rodlike liquid crystalline polymers with a nonlocal intermolecular potential", submitted to Physcial Review E, 2001.